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*Published in:*

The 24th International Congress on Glass - Abstracts

*Publication date:*

2016

[Link to publication from Aalborg University](#)

*Citation for published version (APA):*

Liu, H., Guo, X., Mauro, J. C., & Yue, Y. (2016). Glass transition in mixed network former glasses: Insights from calorimetric measurements. In *The 24th International Congress on Glass - Abstracts* (pp. 120). International Commission on Glass (ICG).

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# Glass transition in mixed network former glasses: Insights from calorimetric measurements

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Modifier-free mixed network former glasses are technically important due to their special properties, e.g., low thermal expansion coefficient, low Young's modulus, and high strain points ( $\geq 650$  °C).<sup>1)</sup> In addition, many mixed network former glasses have high liquidus viscosities ( $>3 \times 10^5$  poise), which is a requirement for the fusion sheet manufacturing process.<sup>2)</sup> Some previous studies have shown the evolution of structural units with composition in ternary network former glasses.<sup>1),2)</sup> Moreover, it has been reported that there is a preference for Al-P instead of B-P association in quaternary network former glasses.<sup>3)</sup> In order to explore the change of the degree of connectivity in mixed network formers with composition, it is highly interesting to study the composition dependent glass transition temperature ( $T_g$ ) of mixed network former glass. Now the questions arise: For this type of glass, how do the thermodynamic properties evolve with composition, such as  $T_g$  and  $C_p$  jump ( $\Delta C_p$ ) during glass transition? By performing calorimetric measurements, can we gain an insight into the degree of distribution of different network formers? In this work, we explore the thermodynamic properties of  $B_2O_3$ - $SiO_2$ - $P_2O_5$ - $Al_2O_3$  mixed network former glasses with a substitution of  $B_2O_3$  for  $SiO_2$  using differential scanning calorimetry (DSC). Figure 1 shows that there are multiple crystallization peaks and two glass transition regions for each sample, and the addition of  $B_2O_3$  causes the number of crystallization peaks increasing and the crystallization temperature decreasing. It has been recently reported the existence of three  $T_g$ s in an ionomer glass.<sup>4)</sup> Although our studied compositions are far away from the immiscible region in the  $B_2O_3$ - $P_2O_5$ - $SiO_2$  phase diagram if  $Al_2O_3$  (4 mol% in all studied glasses) is considered to be replaced by  $B_2O_3$ , two  $T_g$ s exist in all studied glasses, implying the presence of two non-crystalline phases<sup>4)</sup>. As shown in Figure 2, both of the two  $T_g$ s decrease linearly with addition of  $B_2O_3$  content, suggesting that the network would be depolymerized with further addition of  $B_2O_3$ . Moreover,  $T_{g1}$  decreases much faster than  $T_{g2}$ . The different changing rate of two  $T_g$ s may lead to  $T_g$  merging in a critical composition if we extrapolate the linear fitting lines as shown in Figure 2. As a measure of indirect thermodynamic fragility, the  $\Delta C_p$  during the glass transition is calculated. It increases about 20% when  $B_2O_3$  content increasing from 16 mol% to 27 mol%, indicating that the mixed network former liquid becomes more fragile with the increase of  $B_2O_3$  content.

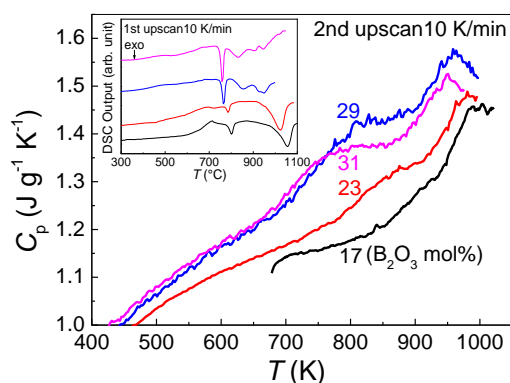


Figure 1. The  $C_p$  curves for the 2<sup>nd</sup> upscan at a heating rate of 10 K/min subsequent to a cooling procedure at the same rate. Inset: DSC output for the 1<sup>st</sup> upscan at a heating rate of 10 K/min.

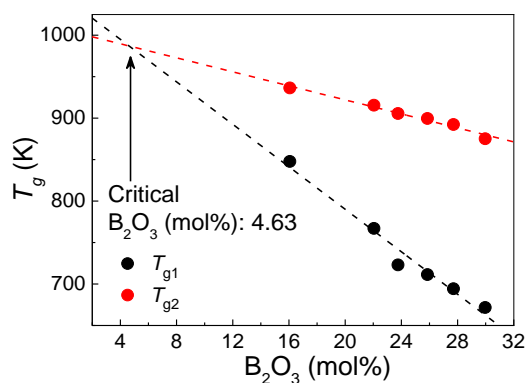


Figure 2. The evolution of  $T_g$  with composition. The dash lines are linear fitting.

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